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Note

X-Ray crystal structure study of zerumbone

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Zerumbone, $C_{15}H_{22}O$, Mr=218.326, monoclinic, P21/c, a=9.039(1)Å, b=9.710(1)Å, c=15.46(2)Å, β=82.78(1)Å, V=1362.3(5)Å, Z=4, Dc=1.065 gm^{-3}, MOKα=0.7093Å, μ=0.600 cm^{-1}, F(000)=480, T=293° K, R=0.061 for 1911 observed reflections. The paper presents three dimensional structure of zerumbone. The structure analysis shows that zerumbone is a big eleven-membered ring and has all-*trans* configuration. The stereo structure of zerumbone has not been reported earlier

We have isolated zerumbone from *Syringa pinnafolia* Hemsl var. *Alashnesis* maets Q. zhou var. nov., collected in the mountainous Helanshan district of north-west China. The accurate molecular weight 218.326 by MS showed the composition to be $C_{15}H_{22}O$ (Calcd 218.334). The IR, UV and NMR data suggest the structure in consistent with that reported by Damodaran & Sukh Dev[1]. Some similar compounds have also been reported[2,3]. But, the X-ray structure analysis of zerumbone has not been reported. Herein we are reporting the structure determination of zerumbone with the help of X-ray single diffraction analysis. It is used as an antipyretic agent in Chinese tranditional medicine, and as a drug for treatment of the symptoms of fever, dizzy and insomnia.

The structure of a single molecule of zerumbone is shown in Figure 1. The atomic coordinates are given in Table I. The bond lengths of O-C1, C2-C3, C10-C11 and C6-C7 are 1.217 (3), 1.317(4), 1.323(4) and 1.377(4) Å, respectively (cf. Table II), indicating that these are all double bonds and their location suggests that there is a conjugated exomethylene moiety. The atoms C1, C2, C3, C6, C7, C10 and C11 are sp^2 hybridized and th3 atoms C4, C5, C8, C9 are sp^3 hybridized. Most of the bond angles in the eleven-membered ring deviate

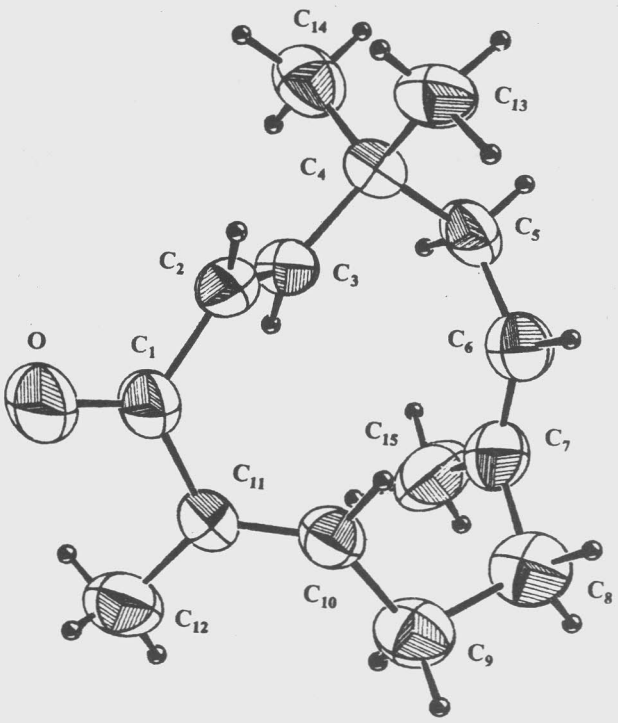

Figure 1.– Molecule draw of zerumbone

from the normal value (cf. Table III). This shows that the eleven-membered ring has a much interior stress which would confer high chemical reactivity on the double bonds. The final X-ray model shows that the molecule has all-*trans* configuration

Experimental Section

The crystal sample recrystallized from hexane had the dimensions 0.3 × 0.3 × 0.5 mm. Enraf-Nonius CAD4 diffractometer was used: Lattice parameters from 25 reflections, with θ = 10-15°; intensities for θ≤26,hkl 0 to 10, 0 to 11, -18 to 18ω-2θ, scan width (0.50 + 0.35 tanθ)°; scan rate 1.0-8.24° /min., extended 25% on each side for background measurement. Three standard reflections (radom variation 2%), LP and absorption correction (7 sample points), transmission factors (0.96-0.99), and 2659 unique reflections were measured; 1911 observations were recorded with I> 3.00(I) where (I)=S+4(B1+B2)+$(0.04S)^2$, S=scan, and B1 and B2 = background counts.

Table I — The atomic coordinates

Atom	*x*	*y*	*z*	B(A2)
O	0.2713(2)	0.4743(3)	0.8507(2)	7.06(7)
C1	0.3973(3)	0.4629(4)	0.8135(2)	4.31(7)
C2	0.5302(3)	0.4600(3)	0.8606(2)	3.98(6)
C3	0.6505(3)	0.5314(3)	0.8325(2)	3.43(5)
C4	0.8020(3)	0.5356(3)	0.8637(2)	3.89(6)
C5	0.9174(3)	0.5410(4)	0.7812(2)	4.79(7)
C6	0.8840(3)	0.4374(4)	0.7142(2)	4.38(7)
C7	0.8360(3)	0.4647(4)	0.6386(2)	4.56(7)
C8	0.7764(4)	0.3515(4)	0.5865(2)	5.21(8)
C9	0.6052(4)	0.3572(4)	0.5914(2)	5.15(8)
C10	0.5382(3)	0.3748(3)	0.6833(2)	3.88(6)
C11	0.4279(3)	0.4551(3)	0.7172(2)	3.81(6)
C12	0.3289(4)	0.5404(4)	0.6675(2)	5.66(8)
C13	0.8273(4)	0.4107(4)	0.9193(2)	5.40(8)
C14	0.8163(4)	0.6678(4)	0.9158(2)	5.62(8)
C15	0.8252(5)	0.6059(4)	0.6030(2)	7.0(1)
H2	0.528(3)	0.398(3)	0.908(2)	4.0*
H3	0.643(3)	0.593(3)	0.783(2)	4.0*
H5A	1.003(3)	0.531(3)	0.796(2)	4.0*
H5B	0.918(3)	0.654(3)	0.758(2)	4.0*
H6	0.885(3)	0.333(3)	0.733(2)	4.0*
H8A	0.817(3)	0.351(3)	0.530(2)	4.0*
H8B	0.805(3)	0.260(3)	0.609(2)	4.0*
H9B	0.584(3)	0.421(3)	0.562(2)	4.0*
H9A	0.565(3)	0.267(3)	0.566(2)	4.0*
H10	0.590(3)	0.318(3)	0.719(2)	4.0*
H12A	0.357(3)	0.546(3)	0.617(2)	4.0*
H12B	0.246(3)	0.516(3)	0.679(2)	4.0*
H12C	0.323(3)	0.660(3)	0.687(2)	4.0*
H13C	0.819(3)	0.313(3)	0.888(2)	4.0*
H13A	0.765(3)	0.405(3)	0.969(2)	4.0*
H13B	0.926(3)	0.407(3)	0.932(2)	4.0*
H14B	0.744(3)	0.677(3)	0.970(2)	4.0*
H14C	0.916(3)	0.684(3)	0.926(2)	4.0*
H14A	0.797(3)	0.747(3)	0.882(2)	4.0*
H15C	0.868(3)	0.689(3)	0.632(2)	4.0*
H15A	0.728(3)	0.648(3)	0.607(2)	4.0*
H15B	0.858(3)	0.618(3)	0.549(2)	4.0*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$(4/3)\times[a^2B_{11}+b^2B_{22}+c^2B_{33}+abB_{12}\cos\gamma+acB_{13}\cos\beta+bcB_{23}\cos\alpha]$

Table II—Bond distances (Å)

O-C(1)	1.217(3)	C(5)-C(6)	1.510(5)
C(1)-C(2)	1.487(4)	C(6)-C(7)	1.337(4)
C(1)-C(11)	1.500(4)	C(7)-C(8)	1.508(5)
C(2)-C(3)	1.317(4)	C(7)-C(15)	1.488(5)
C(3)-C(4)	1.511(4)	C(8)-C(9)	1.541(5)
C(4)-C(5)	1.556(4)	C(9)-C(10)	1.499(4)
C(4)-C(13)	1.526(5)	C(10)-C(11)	1.323(4)
C(4)-C(14)	1.535(5)	C(11-C(12)	1.505(5)

Table III — Bond angles (Å)

O-C(1)-C(2)	122.0(3)	C(4)-C(5)-C(6)	112.4(3)
O-C(1)-C(11)	121.9(3)	C(5)-C(6)-C(7)	126.7(3)
C(2)-C(1)-C(11)	116.0(2)	C(6)-C(7)-C(8)	120.7(3)
C(1)-C(2)-C(3)	120.6(3)	C(6)-C(7)-C(15)	123.9(3)
C(2)-C(3)-C(4)	130.5(3)	C(8)-C(7)-C(15)	115.1(3)
C(3)-C(4)-C(5)	105.9(2)	C(7)-C(8)-C(9)	111.8(3)
C(3)-C(4)-C(13)	111.7(3)	C(8)-C(9)-C(10)	109.5(3)
C(3)-C(4)-C(14)	109.5(3)	C(9)-C(10)-C(11)	130.1(3)
C(5)-C(4)-C(13)	111.5(3)	C(1)-C(11)-C(10)	117.8(3)
C(5)-C(4)-C(14)	108.6(3)	C(1)-C(11)-C(12)	116.4(3)
C(13)-C(4)-C(14)	109.5(3)		

The structure was solved by direct method using the program RANTAN (Jiaxing Yao, 1981), and refined by block and full-matrix least-squares calculations on $|F|$'s. Anisotropic thermal parameters were allowed for non-hydrogen atom. All H atoms were located from a successful difference map and included in structure factor calculations and refined. With fixed isotropic thermal factor to 4.0, the final R=0.068, Rw=0.057 (unit weight), S=0.102; 1911 observations with $I \geq 3.00(I)$, 233 variables; convergence indicated by max. (Δ/δ)=0.76, final difference map showed that the highest peak was 0.252e/Å^3. All the calculations were performed on a PDP11/44 computer using Nonius CAD4-SDP software package (1985). Atom scattering factors were taken from international tables for X-ray crystallography (1974).

References

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